# Estimating the 95th Percentile of the Paste-Void Spacing Distribution in Hardened Cement Paste Containing Air Entrainment

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# ESTIMATING THE 95 th PERCENTILE OF THE PASTE-VOID SPACING DISTRIBUTION IN HARDENED CEMENT PASTE CONTAINING AIR ENTRAINMENT

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## Abstract

The spacing equations of Powers, Philleo, and Pleau and Pigeon are used to estimate the uniform thickness of paste surrounding entrained air voids that is required to encompass 95 % of the air-paste system. Spacing equation accuracy is determined by comparison to the numerically exact result of Lu and Torquato. The air void system is approximated by spheres with radii from a lognormal distribution. For the systems studied here, both the Philleo and the Pleau and Pigeon equations are accurate to within approximately 10 %. The Powers spacing factor can be used to estimate the same quantity to within a factor of two, and could be made far more accurate by adjusting the result using the variance in the air void radius distribution.

## 1 Introduction

The concept of the protected paste volume (PPV) of cement paste containing air entrainment was originally proposed by Larson et al. [1]. The concept disregards the microscopic mechanism of freezing in porous media and considers only the resulting hydraulic forces. Since it was known that the presence of microscopic air voids can significantly reduce the effects of freezing and thawing by acting as pressure release valves, the closer an element of paste was to an air void, more likely the element would not suffer damage upon freezing. Therefore, for two concretes with the same volume of air voids, the concrete with a larger fraction of its paste within a given distance of an air void surface should be more immune to the effects of freezing and thawing. This is the basis for the purely geometrical approach to freeze thaw protection in concrete.

A number of equations exist to estimate the fraction of paste within a given distance

of an air void surface. The first approximation was the Powers spacing equation [2]. Although the microstructural model used (cubic lattice of air voids) was crude, the results were quite reasonable. The first direct calculation of the PPV was by Philleo [3]. Although this equation was published in 1983, Philleo had derived it sometime early, and was used in the paper by Larson et al. [1]. Subsequent equations by Attiogbe [4] and Pleau and Pigeon [5] also attempted to quantify the spacing of air voids in concrete. However, some equations estimate the PPV (paste-void distances) and one estimates void-void distances, and all the equations are only approximations to the true value.

In a previous study by Snyder [6], computer simulation was used to quantify the accuracy of the spacing equations from Powers [2], Philleo [3], Attiogbe [4], and Pleau and Pigeon [5]. The computer program calculated both paste-void and void-void distances for comparison to the spacing equation predictions. However, due to the complexity of the numerical simulation, only monosized spheres and a single lognormal sphere radius distributions were considered.

In addition to the known air void spacing equations, an equation by Lu and Torquato [7] was also considered in the previous experiment. This equation is based upon both Monte Carlo calculations and an analysis of $n$-point correlation functions. For the air void systems used in the previous study, the Lu and Torquato predictions for both paste-void and void-void distances were within the statistical error of the numerical results. Therefore, for tests of air void spacing equations, the Lu and Torquato equations are sufficiently exact to obviate the need for further computer simulation.

For this report, the study by Snyder [6] is extended by using the lognormal distribution with a range of parameter values. Instead of a numerical test, the results from the air void spacing equations will be compared to the results of the Lu and Torquato equation. Also, this study shall be limited to analyzing paste-void distances. The void-void spacing distribution is not studied here for the sake of brevity. Therefore, the Attiogbe equation is not included in this study.

## 2  Air-Paste System

For this study, the conceptual model is simplified by the absence of aggregates. Specifically, the model system is a two-component system composed of air voids and paste. This should be reasonable since the air void spacing equations were developed using the same model. Realistically, this model assumes that the inter-aggregate distance in actual concrete is sufficiently large so as to contain a representative number of air voids, and that the paste-void spacing distribution of this region is representative, on average, of the entire air-paste system.
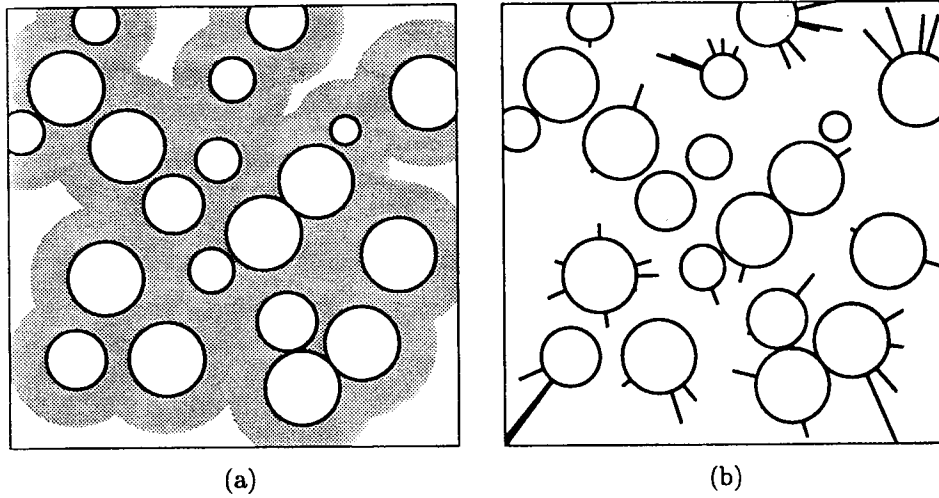
<div align="center">(a)          (b)</div>

Figure 1: A two-dimensional schematic of the paste-void proximity.

## 3 Paste-Void Spacing Distribution

The paste-void spacing equations studied here attempt to estimate the volume fraction of paste within a distance $s$ from the surface of any air void. The spacing equation of Philleo and the equation of Pleau and Pigeon both attempt to estimate this quantity explicitly. The Powers spacing factor simply attempts to estimate some undefined large percentile of this distribution [6].

Equivalent definitions of the paste-void spacing distribution are shown in Figure 1 using two-dimensional representations of quantities measured in three-dimensions. In Figure 1(a) the voids, represented by circles, are surrounded by a uniformly thick gray shell. For a shell of thickness $s$, the area fraction of grey space outside the voids is the fraction of paste within $s$ of a void. This is an intuitive description of the paste-void spacing probability function. At $s = 0$, the fraction is zero. As $s$ increases, the fraction of the paste within $s$ approaches unity asymptotically.

The schematic in Figure 1(b) represents the description of the paste-void spacing distribution most often used in mathematical derivations. In Figure 1(b), points in the paste are chosen at random and the distance to the nearest air void surface is recorded for each point. The number fraction of distances less than $s$ is an estimate of the fraction of paste within $s$ of an air void surface.

In order to evaluate the performance of the various spacing equations, it will be necessary to establish how well they estimate the paste-void probability distribu-

tion. To simplify this task, the equations will only be used to estimate the 95-th percentile of the paste-void spacing distribution. This approach has a number of advantages: the task of quantifying performance is reduced to the comparison of pure numbers; the 95-th percentile is sufficiently large enough to be rigorous since the probability function is "flat" in this region; and the concept of encompassing 95 percent of the paste is intuitive.

## 4 Spacing Equations

A detailed discussion of the following spacing equations has been given previously [6]. The spacing equations are only summarized here.

### 4.1 Nomenclature
Nomenclature for air void quantities differs among authors. To express these quantities with a common notation, the following definitions are given:

$n$ : number of air voids per unit volume.
$A$ : air void volume fraction.
$p$ : paste volume fraction.
$\alpha$ : specific surface area of spheres.
$r$ : sphere radius.
$f(r)$ : sphere radius probability density function.
$\langle R^k \rangle$ : the expected value of $R^k$ for the radius distribution.
$s$ : spacing distribution parameter.

For the paste-air systems considered here, some of these quantities can be defined analytically as follows:

$$A = \frac{4\pi}{3} n \langle R^3 \rangle \tag{1}$$

$$p = 1 - A \tag{2}$$

$$\alpha = \frac{4\pi n \langle R^2 \rangle}{\frac{4\pi n}{3} \langle R^3 \rangle} \tag{3}$$

$$\langle R^k \rangle = \int_0^\infty r^k f(r) \, dr \tag{4}$$

### 4.2 Powers Equation
The Powers spacing factor [2] was developed using two idealized systems. For small values of the ratio $p/A$, there is very little paste for each air void. Powers used the "frosting" approach of spreading all of the paste in a uniformly thick layer over each air void. The thickness of this "frosting" is approximately equal to the ratio

of the volume of paste to the total surface area of air voids:

$$\overline{L} = \frac{p}{4\pi n \langle R^2 \rangle} = \frac{p}{\alpha A} \qquad p/A < 4.342 \qquad (5)$$

For large values of $p/A$, Powers used the cubic lattice approach. The spheres are placed at the vertices of a simple cubic array. The air voids are monosized, each with a specific surface area equal to the bulk value. The cubic lattice spacing is chosen such that the air content equals the bulk value. The resulting Powers spacing factor is the distance from the center of a unit cell to the nearest air void surface:

$$\overline{L} = \frac{3}{\alpha} \left[ 1.4 \left( \frac{p}{A} + 1 \right)^{1/3} - 1 \right] \qquad p/A \geq 4.342 \qquad (6)$$

The $p/A$ value of 4.342 is the point at which these two equations are equal.

The intent was that a large fraction of the paste should be within $\overline{L}$ of an air void surface. An acceptable value of $\overline{L}$ for good freeze-thaw performance was determined from estimating material properties of concrete.

### 4.3 Philleo Equation

Philleo [3] extended the approach of Powers by attempting to quantify the paste-void spacing distribution directly. Philleo started with an idealized air void system composed of randomly distributed points. The probability density for the distance $x$ from a random point in the paste to the nearest zero-radius void is the Hertz [8] distribution:

$$h(x) = 4\pi n \, e^{-\frac{4}{3}\pi n x^3} \qquad (7)$$

Philleo then modified this distribution to accommodate finite-sized spheres by renormalizing the cumulative distribution using the air content. The result is an equation that estimates the paste-void proximity distribution for finite-sized air voids. For the air-paste systems used here, the Philleo spacing factor for the volume fraction of paste within a distance $s$ of an air void surface is a function of the number density of voids $n$ and the volume fraction of paste $p$:

$$F(s) = 1 - \exp \left[ -4.19x^3 - 7.80x^2 \left[ \ln(1/p) \right]^{1/3} - 4.84x \left[ \ln(1/p) \right]^{2/3} \right] \qquad (8)$$

Here, the substitution $x = sn^{1/3}$ has been made.

### 4.4 Pleau and Pigeon Equation

Pleau and Pigeon [5] have recently proposed a spacing equation for the paste-void spacing distribution. Their approach is based on a joint probability distribution function:

$$k(s) = \int_0^\infty f(r) \, h(r+s) \, \Theta(r+s) \, dr \qquad (9)$$

The function $f(r)$ is the air void radius distribution. The function $h(x)$ is the probability density of finding a point in the paste that is a distance $x$ from the center of an air void. The Heaviside function $\Theta(r+s)$ [9] ensures that the argument of the function $h$ remains positive.

As an approximation for $h$, Pleau and Pigeon used the probability density function for the nearest neighbor distance between random points. This is the Hertz distribution given in Eqn. 7. This approximation is equivalent to approximating the air void system by overlapping spheres. The consequence of using the overlapping sphere approximation is an inaccurate estimate of air void volume.

The cumulative distribution function of Eqn. 9 above gives the fraction of the entire system within $s$ of an air void surface:

$$K'(s) = \int_{-\infty}^{s} k(s')\,\mathrm{d}s' \qquad (10)$$

The fraction of paste that is within $s$ of an air void surface is simply the normalized integral over the paste volume:

$$K(s) = \frac{1}{p} \int_{0}^{s} k(s')\,\mathrm{d}s' \qquad (11)$$

Pleau and Pigeon used $1 - K'(0)$ as the normalization factor in their original paper. However, it was pointed out in the Discussion [10] that $K'(0)$ is the air content of overlapping spheres. For the present study, the paste volume $p$ will be used to normalize the equation because results from the previous study by Snyder [6] demonstrated that using the paste content as the normalization factor gave more accurate estimates of larger percentiles of the paste-void spacing distribution.

### 4.5 Lu and Torquato Equation

The Lu and Torquato equation used here was developed using results from both Monte Carlo simulations and an analysis of $n$-point correlation functions. First, Torquato et al. [11] obtained exact expansions of $n$-point correlation functions for simulations of monosized spheres. Next, Lu and Torquato [12] developed a means to map these correlation functions to systems of polydispersed sphere radii. Finally, Lu and Torquato [7] used these mappings to approximate simulation results for polydispersed spheres. It is this equation that is used in this study.

The Lu and Torquato equation requires a number of preliminary quantities [7]:

$$\xi_k \;=\; \frac{\pi}{3} n 2^{k-1} \langle R^k \rangle \qquad (12)$$

$$c \;=\; \frac{4 \langle R^2 \rangle}{1 - A} \qquad (13)$$

$$d = \frac{4\langle R \rangle}{1 - A} + \frac{12\xi_2}{(1 - \xi_3)^2}\langle R^2 \rangle \qquad (14)$$

$$g = \frac{4}{3(1 - A)} + \frac{8\xi_2}{(1 - A)^2}\langle R \rangle + \frac{16}{3}\frac{B\xi_2^2}{(1 - A)^3}\langle R^3 \rangle \qquad (15)$$

The value of $B$ depends upon the way the system was constructed. For the systems used here, $B = 0$. Also, there was a typographical error in the published value for $g$ that has been corrected here. Using these quantities, the fraction of paste within a distance $s$ of an air void surface is an algebraic equation [6]:

$$E_v(s) = 1 - \exp\left[-\pi n \left(cs + ds^2 + gs^3\right)\right] \qquad (16)$$

## 5  Air Void Radii Distribution

This study uses the zeroth-order logarithmic distribution because it is a reasonable representation of air void radii in concrete. The distribution is characterized by the modal radius $r_o$ and the dispersion parameter $\sigma_o^2$ [13]:

$$f(r) = \frac{\exp\left[-\frac{1}{2}\left(\frac{\ln(r/r_o)}{\sigma_o}\right)^2\right]}{\sqrt{2\pi}\,\sigma_o\,r_o\,\exp(\sigma_o^2/2)} \qquad (17)$$

The distributions used in this study are shown in Figure 2. However, the figure contains the corresponding diameter distributions since they are more easily associated with chord lengths obtained from linear traverses.

## 6  Results

The performance of the spacing equations is quantified by the accuracy with which they predict the 95-th percentile of the paste-void spacing distribution. The estimate by Lu and Torquato is considered the most accurate value: $s_{95} = E_v^{-1}(0.95)$. The accuracy of the remaining spacing equations is quantified by the ratio of this value to the Lu and Torquato value $s_{95}$. For Powers, Philleo, and Pleau and Pigeon, these ratios are, respectively:

$$Q_{\overline{L}} = \frac{\overline{L}}{s_{95}} \qquad Q_F = \frac{F^{-1}(0.95)}{s_{95}} \qquad Q_K = \frac{K^{-1}(0.95)}{s_{95}} \qquad (18)$$

Also, the results are given as a function of air content for the paste-air system. The corresponding air content for concrete would be approximately one third of this value.

There is one additional air void radius distribution used in this study that is not shown in Figure 2. This is a monosized radius distribution that corresponds to $r_o = 0.100$, $\sigma_o = 0$.
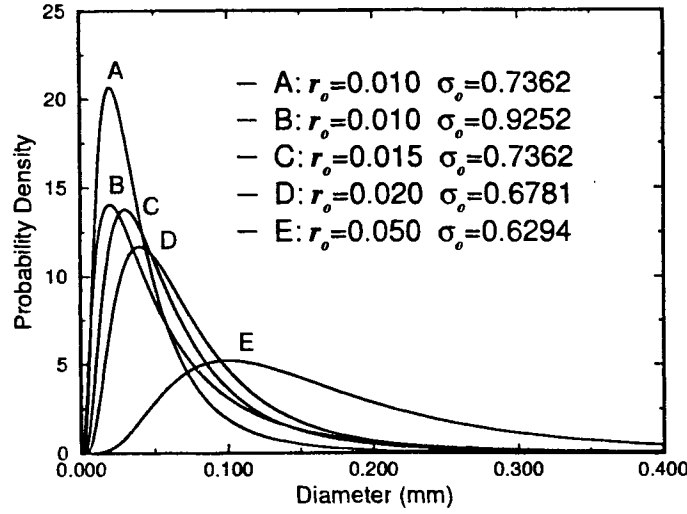
Figure 2: Air void radius distributions.

The values of $Q_{\overline{L}}$ for the Powers spacing equation are shown in Table 1. The results indicate that $Q_{\overline{L}}$ for the Powers equation is a function of only the air content $A$ and $\sigma_o$; the values are not a function of $r_o$. The minimum value for $Q_{\overline{L}}$ is nearly unity for monosized spheres, and it increases to a value near two for the distributions used here. Note also that the *non sequitur* values for the 0.21 air content are due to the use of Eqn. 5.

The values of $Q$ for the Philleo and the Pleau and Pigeon spacing equations are shown in Tables 2 and 3, respectively. These two equations have similar results. Over most of the parameter space investigated, the equations are typically within 10 % of $s_{95}$. Near the limits of the parameter space, the equations are still within approximately 20 % of $s_{95}$. Also, as was true for the Powers spacing equation, the value of $Q$ is only a function of $\sigma_o$ and $A$, and not a function of $r_o$.

The fact that all three spacing equations are only functions of $\sigma_o$ and $A$ means that each equation can be corrected given this information. One could perform a parametric study of linear traverse data, determine the corresponding parameters of the sphere radius distribution, and calculate $\sigma_o$. This, along with the air content $A$, could be used to establish an accurate estimate for $s_{95}$.

Upon reflection, it is not surprising that both the Philleo and the Pleau and Pigeon spacing equations can accurately predict the 95-th percentile of the paste-void spac-

Table 1: Values of $Q_{\overline{L}}$ for the Powers spacing equation.

| $r_o$ (mm) | $\sigma_o$ | $\alpha$ (mm$^{-1}$) | $Q_{\overline{L}}$ Air Content | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 0.06 | 0.09 | 0.12 | 0.15 | 0.18 | 0.21 |
| 0.100 | 0.0000 | 30 | 1.028 | 1.060 | 1.093 | 1.128 | 1.165 | 1.113 |
| 0.050 | 0.6294 | 15 | 1.360 | 1.370 | 1.386 | 1.406 | 1.430 | 1.349 |
| 0.020 | 0.6781 | 30 | 1.428 | 1.434 | 1.446 | 1.464 | 1.485 | 1.397 |
| 0.010 | 0.7362 | 45 | 1.522 | 1.522 | 1.530 | 1.544 | 1.562 | 1.465 |
| 0.015 | 0.7362 | 30 | 1.522 | 1.522 | 1.530 | 1.544 | 1.562 | 1.465 |
| 0.010 | 0.9252 | 15 | 1.965 | 1.941 | 1.928 | 1.925 | 1.927 | 1.791 |

Table 2: Values of $Q_F$ for the Philleo spacing equation.

| $r_o$ (mm) | $\sigma_o$ | $\alpha$ (mm$^{-1}$) | $Q_F$ Air Content | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 0.06 | 0.09 | 0.12 | 0.15 | 0.18 | 0.21 |
| 0.100 | 0.0000 | 30 | 1.076 | 1.115 | 1.155 | 1.196 | 1.240 | 1.285 |
| 0.050 | 0.6294 | 15 | 0.958 | 0.970 | 0.985 | 1.004 | 1.024 | 1.048 |
| 0.020 | 0.6781 | 30 | 0.944 | 0.952 | 0.965 | 0.980 | 0.998 | 1.018 |
| 0.010 | 0.7362 | 45 | 0.926 | 0.931 | 0.940 | 0.952 | 0.967 | 0.984 |
| 0.015 | 0.7362 | 30 | 0.926 | 0.931 | 0.940 | 0.952 | 0.967 | 0.984 |
| 0.010 | 0.9252 | 15 | 0.874 | 0.867 | 0.865 | 0.867 | 0.872 | 0.878 |

ing distribution. Observing Figure 1(a), as the thickness of the shell surrounding the voids increases, the region within the shells begins to resemble a system of overlapping circles, which is the basis of their derivations. This is why the Philleo and the Pleau and Pigeon equations are more accurate at predicting larger percentiles of the paste-void spacing distribution [6].

# 7 Summary

Using a numerically exact equation by Lu and Torquato, the performance of the spacing equations by Power, Philleo, and Pleau and Pigeon is quantified from their estimate of the paste-void spacing distribution 95-th percentile. The results are given as a ratio $Q$ of the predicted value to the true value. For all three equations, the value of $Q$ was a function of the air content and the variance of the air void radius distribution. The ratio $Q$ for the Powers spacing factor $\overline{L}$ was

Table 3: Values of $Q_K$ for the Pleau and Pigeon spacing equation.

| $r_o$ (mm) | $\sigma_o$ | $\alpha$ (mm$^{-1}$) | $Q_K$ Air Content | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 0.06 | 0.09 | 0.12 | 0.15 | 0.18 | 0.21 |
| 0.100 | 0.0000 | 30 | 1.074 | 1.108 | 1.140 | 1.169 | 1.196 | 1.221 |
| 0.050 | 0.6294 | 15 | 1.080 | 1.098 | 1.111 | 1.123 | 1.134 | 1.146 |
| 0.020 | 0.6781 | 30 | 1.072 | 1.085 | 1.096 | 1.106 | 1.115 | 1.125 |
| 0.010 | 0.7362 | 45 | 1.061 | 1.070 | 1.077 | 1.084 | 1.091 | 1.099 |
| 0.015 | 0.7362 | 30 | 1.061 | 1.070 | 1.077 | 1.084 | 1.091 | 1.099 |
| 0.010 | 0.9252 | 15 | 1.022 | 1.020 | 1.017 | 1.016 | 1.016 | 1.018 |

within a factor of two over the parameter space investigated. With the exception of monosized spheres, both the Philleo and the Pleau and Pigeon equations were accurate to within approximately 10 % of the true value over the parameter space investigated.

These results have consequences for research and practice. The PPV can be calculated very accurately using the Lu and Torquato equation, or can be approximated quite well using either the Philleo equation or the Pleau and Pigeon equation. However, each of these equations require the number density of air voids in the concrete, and desire of the PPV may initiate research on accurate methods to attain this quantity. Equally, one may be able to obtain sufficient information from the linear traverse chord distribution to 'correct' the Powers spacing equation to obtain an accurate estimate of the distance from each air void surface that encompasses 95 percent of the paste.

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